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Study of the Recrystallisation of Aluminium/Alumina (SAP) Alloys

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The influence of the introduction of aluminium nuclei on the recrystallisation behaviour of SAP (sintered aluminium powder) was studied by metallographic observations using a new etching reagent, and by transmission electron microscopy. It was observed that the artificial nuclei can grow in the SAP matrix only in the temperature range in which the alloy recrystallises spontaneously. It is concluded that the physical process inhibited by the dispersed particles is grain-boundary migration.

These results and those previously reported confirm Cahn's theory (which regards the formation of new grains as due to recovery phenomena localised in the regions of highest lattice distortion) supplemented by the coalescence mechanism proposed by Hu and Li. Moreover, the basic concepts of "nucleation" and "growth" currently employed to describe recrystallisation phenomena are critically discussed: it is concluded that a reformulation of these concepts is necessary on the basis of the information obtained by means of the more recent experimental techniques, such as electron microscopy.

1. Introduction

Recrystallisation phenomena in SAP are strongly retarded compared with those which occur in aluminium [1, 2]. In particular, it has been observed that, for a constant degree of deformation, the temperature at which recrystallisation begins increases very rapidly with the oxide content. However, no appreciable influence of the impurity content has been noticed for a given amount of oxide [2].

On the other hand, a detailed analysis of recovery phenomena shows no fundamental differences between SAP and pure aluminium, except for an effect of the impurities on the activation energy for dislocation disentanglement, and except for the fact that recovery phenomena can occur over a wider temperature range owing to the increase of recrystallisation temperature [3].

The problem is now to establish whether the shift of recrystallisation to higher temperatures is caused by the inhibition of nucleation or of growth phenomena.

It is accepted that inclusions inhibit grain-boundary migration, while for nucleation either inhibition or acceleration has been reported, depending on the dimensions and degree of dispersion of the inclusions themselves [4]. Some of our preliminary observations [5], in agreement with a hypothesis formulated by other authors [1], suggest that the orientation of the oxide platelets has an influence on the shape of the recrystallised grains, the growth rate being higher in the direction along which the cross-section of the oxide particles is less.

If the formation of recrystallisation nuclei is associated with a localised recovery process (i.e. the formation and growth of cells more perfect than the surrounding matrix) as is commonly believed, the retardation of recrystallisation in SAP should be attributed to the inhibition of boundary migration, since, as mentioned before, the oxide particles have a minor effect on the recovery processes. In particular, the results of earlier work [3] indicate that the increase of sub-grain size

observed by electron microscopy in the recovery stage preceding recrystallisation (centred at ~300° C) is not due to sub-boundary migration, but to the sub-grain coalescence mechanism proposed by Hu [6] and Li [7]. This process has been observed by Weissmann *et al* in aluminium [8]. In SAP, it is quantitatively more pronounced and the temperature range of the above-mentioned recovery stage increases with the oxide content [2]. This indicates that grain-boundary migration is strongly inhibited by the dispersed phase.

A direct and unambiguous check of the proposition that the dispersed particles have an influence only on the boundary migration rate, and not on the nucleation frequency, would be very important, not only in itself but also because it would give a more solid foundation to the existing general ideas on recovery and recrystallisation phenomena.

Such a crucial test has been suggested to us by Professor R. W. Cahn: one has to introduce some aluminium nuclei and to verify whether they can grow in the cold-worked SAP matrix at a temperature substantially lower than that at which this material recrystallises spontaneously.

2. Experimental

2.1. Specimen Preparation

The observations were carried out on two SAP alloys of different oxide and impurity content, with detailed compositions as reported in table I. To provide the aluminium nuclei for recrystallisation, Al (99.999%)/SAP sandwiches were prepared by diffusion-welding and subsequent rolling. Diffusion-welding was done by heating the slabs, clamped together, at 640° C for 30 min under vacuum (~10^{-6} torr). Then they were cooled very slowly in the furnace. For a successful result in the welding operations, a careful preparation of the two contact surfaces was necessary. We tried several polishing solutions and obtained the best results with that used for thinning SAP samples for electron microscope observations [2]. Particular care was necessary to ensure that the prepared surfaces were exposed to air for as little time as possible.

The sandwiches were then cold-rolled down by reductions of more than 90%, keeping the rolling plane parallel to the plane of the weld. Rolling was obviously the most severe test of good welding; neither separation nor blister formation was observed. For a more detailed check of the welding, the transition region between aluminium and SAP has been examined by transmission electron microscopy. For these observations, it was necessary to operate on samples obtained by transverse rolling of the sandwich (i.e. keeping the rolling plane normal to the plane of the weld) and subsequent thinning.

In order to compare the recrystallisation behaviour of work-hardened samples bearing aluminium nuclei, with others completely identical but for the presence of these nuclei, we proceeded in the following way. All the samples were obtained from the same sheet of cold-rolled sandwiches and from some of them the aluminium layers were taken away, at first mechanically and at the end by means of the above-mentioned electrochemical polishing solution [2].

2.2. Metallography

For the study of recrystallisation phenomena, we carried out observations by optical microscopy. The choice of a suitable metallographical etching reagent gives rise to difficulties in SAP because of some masking effects due to the oxide particles. The etching reagents which display the grain boundaries in aluminium are not effective, probably because of a simultaneous etching at the Al/Al_2O_3 interphase boundaries.

In order to make the use of optical microscopy possible, we tried several different etching reagents [1, 9]. The most satisfactory results have been obtained with a new solution having the following composition: HNO_3 (65%), 24 cm^3; HF (37%), 1 cm^3; HCl (37%), 15 cm^3; H_2O (bi-distilled), 20 cm^3. This reagent is very sensitive to contamination. The most suitable etching temperature is about 50° C. The solution produces etch-pits. The contrast arises

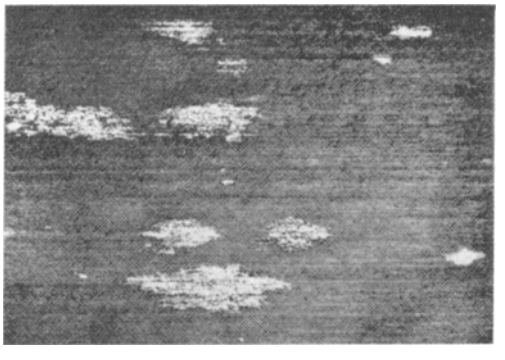


Figure 1 SAP 4.3%. Grains growing in the cold-worked matrix; the latter is darker (×7.3).

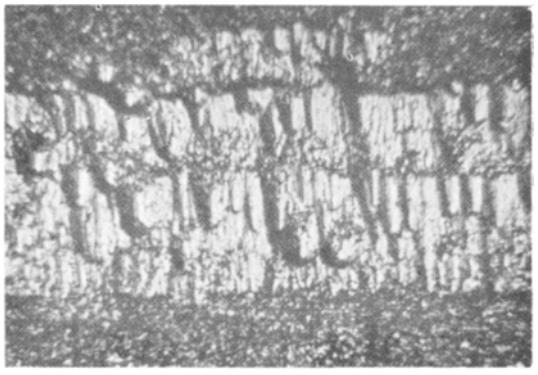


Figure 2 SAP 4.3%. Features of the etch-pits within a crystal and appearance of the unrecrystallised matrix (×1950).

because the deformed matrix is more deeply etched and has a lower reflecting power than the recrystallised grains, which stand in relief. Fig. 1 shows crystals growing in the deformed matrix. Individual grains can be identified owing to the orientation of the etch-pits: fig. 2 shows details of a crystal at high magnification.

In a completely recrystallised sample, by rotating the specimen holder of the microscope under oblique illumination, the different crystals are displayed in turn.

The examination of recrystallisation has been carried out on transverse sections of the cold-rolled and annealed sandwiches; after mounting in resin, the sections were diamond-polished and etched. We have used a Reichert metallographic microscope.

Electron microscopy observations have been carried out by transmission using the techniques described [2, 3] and a Siemens Elmiskope II electron microscope. Single grains have been recognised by extinction-tilting and localised electron diffraction.

2.3. Heat-Treatments

The recrystallisation treatments have been carried out in a molten salt bath (60% $NaNO_3$/ 40% KNO_3) with a temperature stabilisation of $\pm 0.1°$ C. The annealing treatments were carried out for a constant time of 30 min.

3. Results

The transmission electron micrograph in fig. 3 of the welded region in the cold-worked state demonstrates the physical continuity between aluminium and SAP. The welded region seems characterised by a concentration of oxide

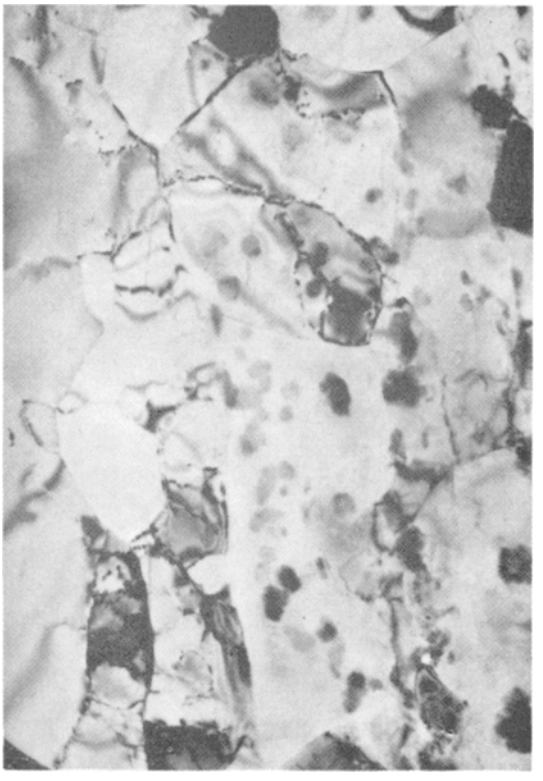


Figure 3 Transmission electron micrograph of the weld between aluminium (left-hand side) and SAP 2.7%; specimen rolled to ~99% reduction (×26 000).

particles decreasing from SAP to aluminium. Our observations indicate that neither an oxide film nor substantial enrichment of alumina occurs in the weld.

Recrystallisation tests on aluminium/SAP sandwiches have been carried out starting from 240° C; at this temperature, aluminium is already completely recrystallised, while SAP does not show any recrystallisation.

For the sake of simplicity, we limit ourselves to reporting in detail the results on SAP with 2.7% oxide, rolled to ~94%; these rolled sandwiches were ~500 μm thick, bearing at the centre, between two symmetric layers of aluminium, an SAP strip about 55 μm thick.

SAP does not present any recrystallisation up to 360° C. Normally, the same is observed at 380° C, as is also illustrated in fig. 4, which shows the polycrystalline matrix of aluminium on both sides of the unrecrystallised strip of SAP. In some rare cases, a beginning of penetration of aluminium crystals in the SAP matrix has been noticed after annealing at this temperature.

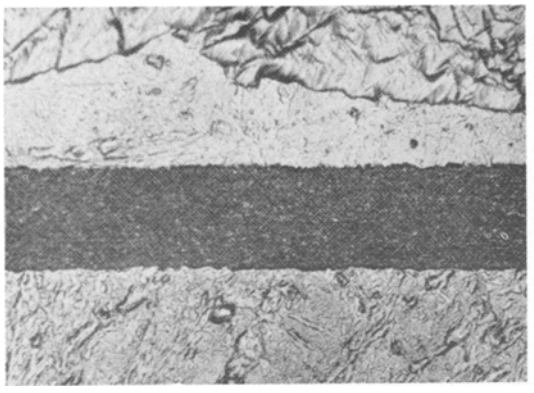


Figure 4 Sandwich Al/SAP 2.7% annealed 30 min at 380° C; the unrecrystallised SAP strip at the centre is darker; transverse section (×240).

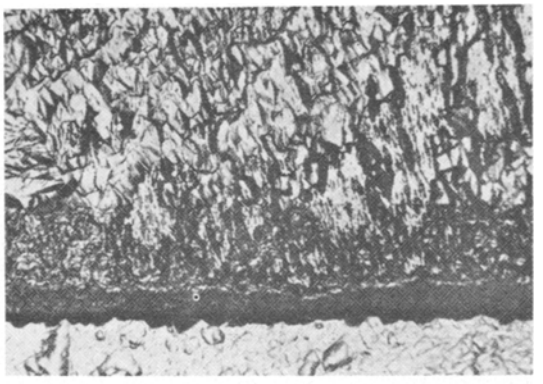


Figure 5 Sandwich Al/SAP 2.7% annealed 30 min at 397° C (×240). Grain growing on from the aluminium into the matrix of SAP; the alloy portion of the grain is recognisable from the different reflecting power. The black contour between SAP and the lower aluminium crystal, which stands in relief, is due to the step due to differential etching; transverse section.

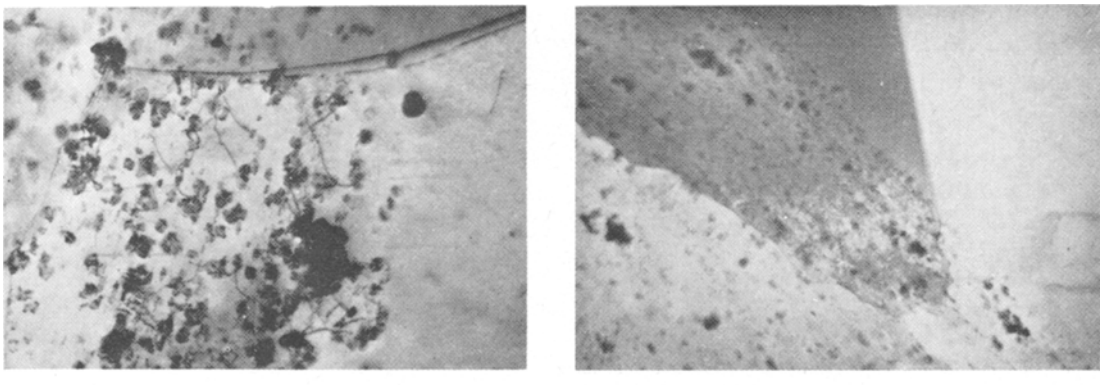
Extensive propagation, however, is observed only above 390° C, and the recrystallisation of the SAP strip is nearly completed at 420° C.

Fig. 5 shows a crystal growing from the aluminium into the matrix of SAP. The orientation of the etch-pits demonstrates that we are dealing with a single crystal; the SAP portion is still clearly recognisable from the different reflecting power. The presence, in the region of the weld, of single grains consisting in part of aluminium and in part of SAP was confirmed by electron microscopic observations of recrystallised specimens. This situation is very common and is illustrated in figs. 6a and 6b.

Another feature of the recrystallisation behaviours of the sandwiches is exemplified in fig. 7: one can observe two aluminium crystals penetrating from both sides of the SAP strip and another one which does not propagate. Systematic observations have shown that the degree of penetration is different for the different aluminium crystals, and this suggests that the growth rate depends on the orientation. The detail shown in fig. 8 clearly illustrates this point.

We note that, since the etching rate depends upon the crystal orientation, steps may be formed at the boundaries between aluminium crystals or amongst these and the SAP strip. These steps appear as dark contours in the micrographs.

Together with the crystals resulting from the propagation of the aluminium grains, crystals



(a) (b)

Figure 6 Transmission electron micrographs in the region of the weld between aluminium and SAP 2.7%. Specimens rolled to 99% reduction and recrystallised: (a) grain boundary crossing the transition region between aluminium (right-hand side) and SAP (×17 700); (b) features of "mixed" Al/SAP grains (×5280).

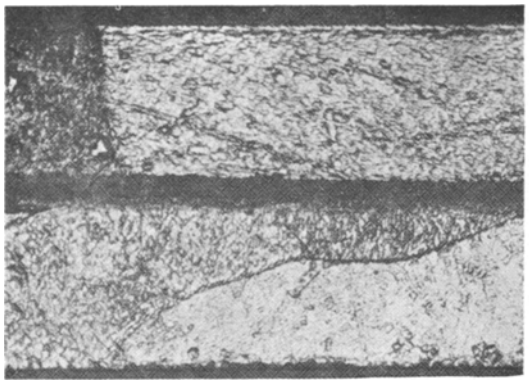


Figure 7 Sandwich Al/SAP 2.7% annealed 30 min at 397° C; penetration of aluminium crystals from both sides of the SAP strip (×90).

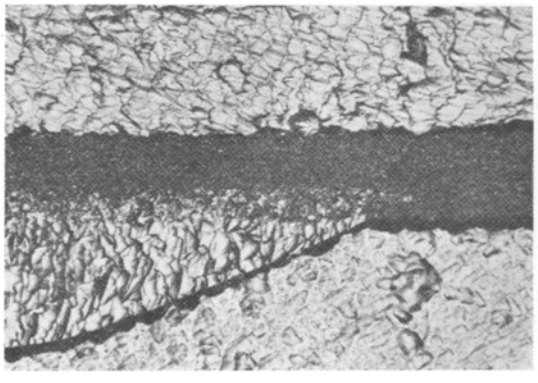


Figure 8 Detail of fig. 7 (right-hand side) showing the different penetration of adjacent aluminium grains; note the steps which are due to differential etching (×240).

originated in the SAP matrix can also be observed in the same specimens: fig. 9 shows a

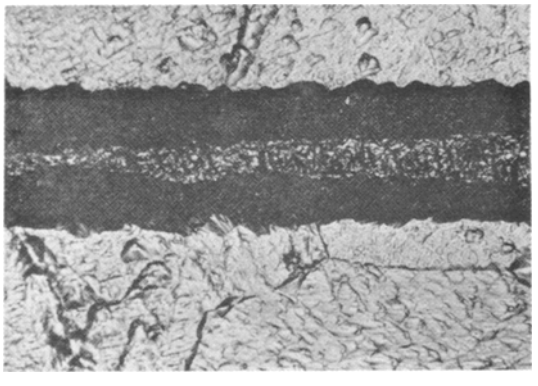


Figure 9 Sandwich Al/SAP 2.7% annealed 30 min at 397° C; centre-grown grain of SAP (×240).

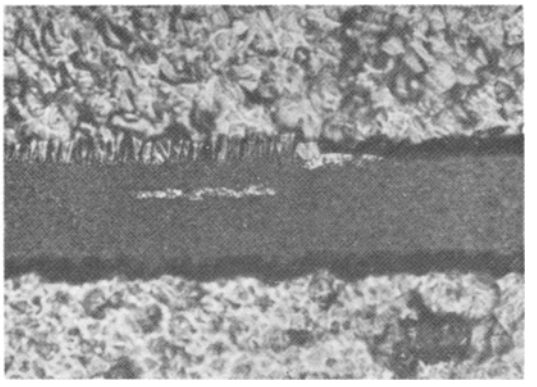


Figure 10 Sandwich Al/SAP 2.7% annealed 30 min at 397° C; initial penetration of an aluminium grain from the upper side of the strip and small centre-growing SAP grain (×240).

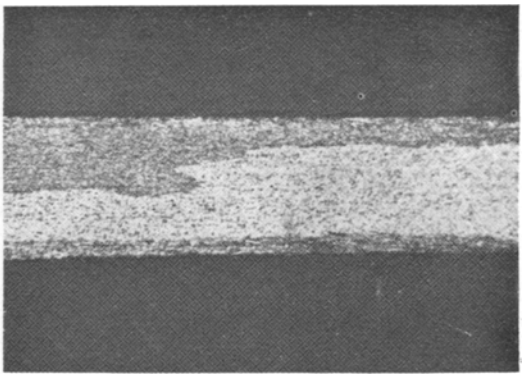


Figure 11 Recrystallisation features of an SAP 2.7% strip deprived of the aluminium and annealed 30 min at 397° C (×320).

centre-grown, large crystal of SAP; fig. 10 shows a small SAP grain, with incipient penetration by an aluminium crystal. This indicates that the growth of aluminium crystals in the matrix of SAP takes place only in the temperature range in which the alloy also recrystallises spontaneously.* This result is confirmed by the examination of the SAP strips deprived of the aluminium "nuclei". Their recrystallisation behaviour is similar to that in the sandwich: also, in these specimens, recrystallisation occurs extensively above 390° C. A typical situation in an SAP strip, annealed at the same temperature as the sandwiches in figs. 5, 7, *et seq*, is shown in fig. 11.

The alloy with 4.3% oxide shows a similar behaviour (i.e. the recrystallisation temperature

*Of course, this temperature depends on the oxide content [2] and the degree of deformation.

TABLE I Composition of alloys (wt %).

Al_2O_3	Fe	Si	Mg	Cu	Zn
2.7	<0.007	0.01	0.006	0.002	0.009
4.3	0.12	≤0.1	≤0.1	0.01	0.006

of SAP is not substantially altered by the presence of the aluminium "nuclei").

4. Discussion

The recrystallisation behaviour of aluminium/SAP sandwiches shows that the increase in recrystallisation temperature of SAP is due to the inhibition of grain-boundary migration.

These results are consistent with the conclusions from earlier work [3], that the sub-grain growth in the recovery stage before recrystallisation (which we called stage B) does not occur through boundary migration, which is inhibited at that temperature, but through an alternative mechanism, probably the sub-grain coalescence mechanism proposed by Hu [6] and Li [7]. Such a process leads to the formation of crystals surrounded by high-angle boundaries.

As already mentioned (see section 1), this mechanism occurs in SAP more abundantly than in aluminium, because its extent depends upon the ratio between the rate of cooperative dislocation climb and that of grain-boundary migration. Therefore the observed phenomena imply a competition between recovery and grain-boundary migration, in agreement with our observations [2, 5] already mentioned, and others which will be reported in a forthcoming publication. This conclusion can explain why, in the experiments on SAP reported by Westerman and Lenel [1], the growth rate decreases with time.

The results of our studies lead us to discuss some conceptual foundations of the theory of recovery and recrystallisation phenomena. The development of experimental techniques such as transmission electron microscopy requires a deep revision of some concepts of traditional metallurgy. We think that terms such as *nucleation* and *growth*, currently used to describe recrystallisation phenomena, should be critically analysed and replaced by less ambiguous terms, more strictly related to the observed physical processes.

In conventional metallography, the *nucleus* is operationally defined through the *nucleation frequency*, which is given by the number of new crystals appearing per unit time (per untransformed unit volume). To indicate this quantity, the term *operational nucleation frequency* [10] would be more suitable, in order to emphasise the fact that it is related to the instrumental resolution of the optical microscope and therefore could result from any of several different physical processes, such as rearrangement of dislocations by cross-slip or climb, sub-grain growth by the coalescence mechanism, or the migration of sub-grain and grain boundaries.

Moreover, growth inhibition can prevent the sub-grains from becoming large enough to be considered as nuclei in the conventional metallographic sense and can therefore affect the experimental value of the operational nucleation frequency.

The concept of *nucleation* acquires intrinsic significance from the concept of *critical radius*. In the classical nucleation theory, this term has a well-defined thermodynamic meaning: when the radius of a nucleus of the new phase is greater than the critical radius, it can grow at the expense of the other phase, whereas the contrary occurs if it is smaller. As Oriani [11] pointed out, this point of view is meaningless in the case of recovery and recrystallisation phenomena: an initial metastable state does not exist and the free energy steadily decreases with decreasing dislocation density. In some theoretical treatments, confusion arises because the fact is not taken into account that, in the initial recovery stage, low-angle boundaries are formed. This means that the surface energy term to be used for the calculation of the critical radius is lower [12]. In other words, as Bollmann pointed out [13], both volume and surface energy depend upon the local dislocation density. As a consequence, one obtains that the critical radius should be of the order of the mean distance between dislocations.

Also the term *growth* carries with it a certain, although less fundamental, ambiguity. In fact, while, on a macroscopic scale, grain growth occurs by boundary migration, on the scale of electron microscope observations, other growth mechanisms can operate, such as Hu and Li's coalescence mechanism.

The foregoing sets out some of the reasons why results of different authors are often poorly comparable [4, 12, 14]. In particular, we note that, although no consistent theoretical justification for this procedure exists, nucleation is frequently treated as a single phenomenon whose

temperature dependence can be expressed by a definite activation energy.

To take an example concerning SAP, Westerman and Lenel [1], in studying operational nucleation frequency, obtained an activation energy for nucleation of 110 kcal/mol. Our experiment shows that the parameter which determines the crystal growth up to a size large enough for them to be considered as metallographical nuclei is the grain-boundary migration rate. Therefore, the operational nucleation frequency is not a suitable physical parameter for the analysis of the thermally activated phenomena preceding boundary migration. In fact, the activation energy value found by Westerman and Lenel does not correspond to any one of the values found for the recovery processes preceding recrystallisation. In particular, the recovery stage immediately preceding boundary migration has an activation energy equal to that for self-diffusion in aluminium [3].

These remarks on SAP can probably be extended to other alloys containing a finely dispersed phase and, in general, to all cases in which boundary migration is relatively more inhibited than dislocation recovery processes [15].*

We must also point out that there is no contradiction between our results and those of Doherty and Martin [16] concerning the recrystallisation of Al/Cu two-phase alloys. These authors observed the formation of grains reaching a size of ~ 1 μm, beyond which they do not grow owing to the presence of the dispersed particles. They concluded that these particles inhibit the nucleation of new grains. The different interpretation arises indeed from the use of the operational nucleation frequency and also from the fact that, at that time, the observations on Hu and Li's coalescence mechanism were at the very beginning.

We note that the possibility of getting unambiguous conclusions from our experiments is due essentially to the fact that recovery and recrystallisation phenomena are better separated in SAP than in pure aluminium. Therefore it is possible that dispersed-phase alloys allow other experiments of this type, aiming at separating the different recovery processes in work-hardened metals.

5. Conclusions

It has been shown that artificial aluminium nuclei, introduced by diffusion-welding, can propagate in SAP only at temperatures at which this material begins to recrystallise spontaneously. This shows that boundary migration is the hindered physical phenomenon.

The whole of our results on recovery and recrystallisation phenomena in SAP [2, 3] are consistent with Cahn's model, which regards the formation of new grains as due to recovery processes localised in the regions of highest lattice distortion [17]; the early stage of sub-grain growth and the formation of high-angle boundaries takes place by the recently suggested sub-grain coalescence mechanism.† These results suggest also a critical analysis of the concepts of nucleation and growth, and a new formulation of these in terms more related to the physical processes which are really observed with the modern experimental techniques.

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*Probably we are dealing here with a general situation, which can explain why equal activation energy values are so often observed for nucleation and growth [14].
†For sake of completeness, we note that Bailey and Hirsch's mechanism [18] does not concern our case, since it is operative only for lower degrees of deformation.

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